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PLATINUM MONOLAYER ON NON-NOBLE METAL - NOBLE METAL CORE-SHELL NANOPARTICLES ELECTRO-CATALYSTS FOR O_2 REDUCTION

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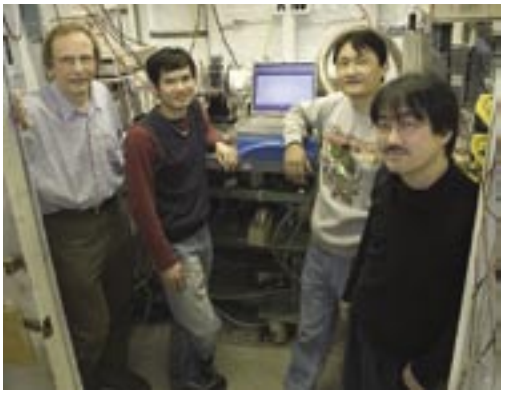
We synthesized a new class of O_2 electrocatalysts for fuel cell cathodes. They consist of a Pt monolayer deposited on carbon-supported nanoparticles that have non-noble-metal cores and noble-metal shells. These nanoparticles were formed from a mixture of noble and non-noble metals. At elevated temperatures, the noble metal moves to the surface, while the non-noble metal remains in the core. The Pt monolayer was deposited onto the nanoparticles by galvanically displacing an adsorbed Cu monolayer. The mass activity of these electrocatalysts is more than an order of magnitude higher than that of commercial Pt/C electrocatalysts. Strain in the Pt monolayer and the reduced coverage of the reaction inhibitor (PtOH), revealed by x-ray absorption spectroscopy data, are the origin of the enhanced catalytic activity.

As the interest in a "hydrogen-based economy" grows, research on its major elements — hydrogen production and storage, and energy conversion in fuel cells — is expanding. While fuel cells are expected to become a major source of clean energy, existing fuel-cell technology still has two drawbacks: energy conversion that is lower than the theoretical efficiency, and electrocatalysts with a high Pt content. Both problems are connected to the rather slow electrocatalytic O_2 reduction reaction (ORR).

Several approaches explored in the past to ameliorate this disadvantage have had limited success. We, however, have demonstrated a promising way to solve these problems. Our method involves electrocatalysts consisting of a Pt monolayer supported on suitable metal nanoparticles. These electrocatalysts have a very high activity and an ultra-low Pt content that promises to alleviate the above problems. Platinum is deposited in a monolayer amount on the surfaces of carbon-supported non-noble metal/noble metal core-shell nanoparticles (**Figure 1**). Using non-noble metals for the cores facilitates a further reduction of the content of the noble metal in the ORR electrocatalysts. In addition, by properly selecting the noble-metal shell, the activity of the Pt monolayer can be heightened through electronic and/or geometric effects. The choice of the metals constituting the shell and core is based on the segregation properties of the two metals, as well as their electronic and strain-inducing effects on the Pt monolayer. The nanoparticles were synthesized by segregating the atoms of the noble metal to the nanoparticle surface at elevated temperatures. A Pt monolayer was then deposited on the nanoparticles via the galvanic displacement by Pt of an adsorbed Cu monolayer.



Authors (from left): Radoslav Adzic, Junliang Zhang, Minhua Shao, and Kotaro Sasaki

The noble-metal shell in the core-shell nanoparticle has two roles. First, it protects the non-noble core from contacting the acid electrolyte, i.e., it precludes its dissolution. Second, the proper shell can improve the catalytic properties of a Pt monolayer by affecting its electronic properties and/or by inducing strain in the monolayer, which increases its activity. A strong surface segregation of the noble metal component is the key feature of these systems. The surface segregation of Au, Pd, and Pt and their protection of the Ni or Co core from dissolution was verified by linear sweep voltammetry, underpotential deposition (UPD) of Cu, and x-ray diffraction techniques. The activity of these electrocatalysts, calculated as the current at 0.85 V divided by the mass of Pt, is about 20 times above that of commercial Pt/C electrocatalysts. If the total noble-metal mass is counted, the activity

is about four times larger. The very high activities appear to be a consequence of a strain that appears due to a mismatch in the lattice constants between the monolayers and these substrates, the changes in the d-band properties of the Pt monolayer itself (caused by its interaction with them), and the decreased PtOH coverage. These effects were observed by *in situ* synchrotron radiation techniques.

In conclusion, we demonstrated the synthesis of a new class of electrocatalysts consisting of a Pt monolayer deposited on non-noble metal/noble metal core-shell nanoparticles. We showed that it is possible to devise ORR electrocatalysts, with activity surpassing that of state-of-the-art carbon-supported Pt electrocatalysts, that contain only a fractional amount of Pt and a very small amount of another noble metal. Consequently, the cost of fuel cells could be lowered considerably. Further work on these systems will address the question of their long-term stability.

Figure 1. Model for the synthesis of Pt monolayer catalysts on non-noble metal-noble metal core-shell nanoparticles.